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COMPLETE SPECIFICATION

Titanium-Containing Non-Ferrous Metal Alloys

We, STOLBERGER ZINK AKTIENGESELLSCHAFT Für Bergbau und Huttenbetrieb, of 37 Theaterstrasse, Aachen, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to alloys of non-ferrous metals containing titanium. More specifically, the invention relates to alloys of zinc, including a minor amount of titanium in which the alloy has been further modified to improve the malleability and other physical properties of the alloy.

One of the most important characteristics of a zinc alloy is its behaviour in the solid state at room temperature when subject to working such as bending, folding, compressing, and drawing. Hexagonal metals such as zinc when subjected to the foregoing manipulations, show a high degree of dependence on the direction of deformation, and are particularly sensitive to stresses caused by changing temperatures during its use in manufacturing or machining. When these metals are worked and subjected to temperature changes, recrystallisation appears in the metal and there is a consequent reduction in ductility of the metal.

There have been numerous attempts to change the behaviour of the metals by the addition of alloying elements. It has been found that small amounts of solid solution forming agents such as minor amounts of magnesium are effective in accomplishing this purpose. While the end product so prepared is fine-grained, it is at the same time tempered so that the plasticity of the alloy is reduced. Primary crystallizing admixtures such as iron (as tempered crystals with zinc) or manganese, have a fine-crystal effect, but the ductility of the alloy is reduced through the formation of large crystallites at the inter-

faces. Aluminium-containing alloys, because of their tendency toward intercrystalline corrosion, remain limited to those made from zinc powder. In addition, their technologically desirable properties are considerably impaired on exposure to heat.

Another approach has been discovered in the field of aluminium research where it has been found that the addition of minor amounts of titanium to aluminium produces a fine-grained crystal structure and results in a suitable degree of malleability and ductility.

It is believed that the initially precipitated aluminium-titanium crystals act as a nucleus during crystallisation. With zinc however, such effects are not obtainable to any suitable extent. Alloys with a eutectic titanium content of about .2% to about .4% titanium are not sufficiently fine-grained to result in a high ductility in the final malleable product.

Attempts have also been made to dissolve the high melting titanium in zinc under vacuum or inert gas but these attempts have also presented numerous difficulties. Similar problems such as lack of sufficiently high ductility are present when alloys of non-ferrous metals other than zinc are prepared by conventional methods.

Other studies on copper-titanium or manganese-titanium in the form of low melting pre-alloys have been made where they were dissolved in zinc. In the study of the influence of copper-titanium, manganese-titanium, or ternary copper-manganese-titanium pre-alloys on the properties of moulded or kneaded zinc bodies, helpful information has been obtained. Thus, if pure metallic titanium with a degree of purity corresponding to a Brinell hardness of 60–80 kg/mm² is melted under vacuum to form a copper-titanium pre-alloy, and if zinc is added to this, an alloy having a relatively finely divided dispersion of titanides is obtained, the alloy having a copper content of 0.5% to 1% and a titanium content of 0.1% to 0.4%. It has been found

that the creep resistance of such alloys is increased, especially when they have been heated to 150—200°C. Unfortunately, with increasing titanium content, the machining properties became worse. See U.S. Patent No. 2,472,402. While the tendency to recrystallise is raised to temperatures higher than normally characteristic of zinc, the plasticity of alloys of this type still does not reach an acceptable value to make it a commercially workable composition.

It is an object of the present invention to provide zinc alloys containing titanium which have improved malleability and other improved physical properties.

According to the present invention, there is provided a titanium zinc alloy which contains more than 50% by weight of zinc, the balance apart from unavoidable impurities being titanium and from 1 to 67 atomic per cent of hydrogen or nitrogen or oxygen or a mixture of two or more of these elements, based on the quantity of titanium, which hydrogen, nitrogen or oxygen is combined with the titanium, is dissolved in the solid solution or is in part combined and in part dissolved.

The outstanding improved properties of the alloys of the invention appear to result from the fact that the alloy contains from 1 to 67% atomic per cent of hydrogen, nitrogen and oxygen, either singly or in admixture based on the titanium content.

Although the invention is not to be considered as limited by any theoretical explanation thereof, it is believed that the improved properties of the alloys may be explained as follows: The titanium when added in pure metallic form forms compounds with the major constituents of the alloy which, depending on the rate of cooling when it is taken out of the mould, exhibits a more or less distinct acicular structure. In the solid state these intermetallic phases possess a definite solvent power for these major constituent(s). During solidification in the mould or during heat treatment in the solid state (for example annealing, hot forming) diffusion reactions occur, which have an important effect on the crystal formation.

It is believed that with increasing saturation of the titanium with hydrogen, nitrogen, or oxygen, singly or in combination, the affinity of the intermetallic phases for the major constituents, and for the various contaminants is decreased. However, while the solubility of the titanium in the alloy decreases the amounts that do go into solution are precipitated in an extremely fine-grained form. These amounts are found not only deposited as part of eutectic mixtures at the interfaces, but also within the crystallites themselves where they act as primary seed crystals.

The affinity of the minor amounts of titanium crystals in the alloy which are bound or in solution with hydrogen, nitrogen or

oxygen is practically zero for the major constituents. The temperature at which they collectively will crystallize lies well above the melting point of the major constituents of the alloy so that neither in gradual cooling outside the moulds nor in any sort of heat treating in the solid state is any change in the fine dispersion produced.

The titaniferous alloys of non-ferrous metals of the present invention differ from the prior art by the presence of the hydrogen, nitrogen, or oxygen, singly or in combination, in the alloy. The structure of the alloy is not restricted to any particular arrangement. Thus, the titanium in the alloy may be wholly or partly bound to the hydrogen, nitrogen, or oxygen or mixtures thereof. Equally well these latter three elements may be present in the form of solid solutions with the titanium or as a saturated hydride, nitride, or oxide.

The alloys according to the present invention may advantageously contain, besides the titanium, the zinc and the hydrogen, nitrogen, or oxygen, 0.1% to 10% copper as well as 0.1% to less than 50% aluminium. Advantageously 0.05% manganese may also be present. Also, up to 50% of the copper when present may be replaced by manganese. It has also been found that no more than 50% of the titanium, which is preferably present in an amount of 0.01% to 1% by weight of the alloy, may be replaced by zirconium and/or hafnium.

Some of the more outstanding advantages of the alloys of the present invention may be summarized as follows: The fine-grain characteristics are relatively permanent throughout hot processing and heat treating of every type of alloy primarily due to the heightened temperature of recrystallization which is raised beyond the melting point. The alloys are of high quality for hot- and cold-working processes, without reference to the critical degree of deformation, since no critical temperature is present in the soft annealing process. The alloys have high creep resistance, especially zinc base alloys containing copper and/or aluminium besides the titanium. The alloys have excellent bearing characteristics because of the finely divided crystals of the titanium-nitrogen, the titanium-hydrogen or the titanium-oxygen combination. They have excellent working, bending and deep drawing properties, and are resistant to inter-crystalline corrosion because the interfaces are blocked by resistant titanium phases.

The alloys of the present invention are made by techniques well known in the art for the manufacture of alloys with the additional step of introducing nitrogen, hydrogen, or oxygen, singly or in combination into the alloy product. The manufacture of the alloys may take place directly from the component elements or by way of pre-alloys. Thus, in the preparation directly from the component ele-

ments the melting process may be carried out in the presence of a suitable gas containing the element desired to be introduced into the alloy. Thus nitrogen may be introduced directly, and when hydrogen is to be introduced, hydrogen gas and/or ammonia may be employed. Mixtures of appropriate gases are used when mixtures of the elements are to be introduced.

When pre-alloy techniques are to be used, the titanium may be separately combined with nitrogen, hydrogen, or oxygen and then combined with the melt, or both the titanium and the melt individually may be treated with the appropriate gas and then combined.

Zinc alloys based on high purity zinc and zinc spelter have been studied in connection with the present invention, and it has been found that high purity zinc or zinc spelter or mixtures thereof are suitable for purpose of the present invention. In this respect the use of grades of zinc (spelter) which have a lead content of over 0.1% has hitherto been considered unsuitable for such alloys since inter-crystalline corrosion has appeared. However, according to the present invention splatters containing up to 1.5% lead may be employed.

In addition, alloys have been investigated which contain from 0.1% up to 10%, preferably up to 2% copper and from 0.01% up to 1% titanium as well as quaternary alloys with an admixture of from 0.05% up to 1.5% manganese. In all cases, the alloys were

cast in ingots which were rough treated hot at 250°C. and were worked into sheet metal 0.6 mm. thick at about 20—100°C., preferably between 50 and 80°C.

The alloys were tested by studying their bending behaviour as compared with the materials indicated which are normally obtainable commercially. Comparisons were made by reference to a bend-test number. This refers to the number of bendings to and fro that occur before fracture of the material sets in. In the Examples 1 to 3 given below, which are by way of illustration only all results refer to an alloy having about 0.6% copper and from 0.05 to 1% titanium, in addition to zinc as the major constituent. In Example 4 which is also by way of illustration only, the creep resistance of certain high purity zinc alloys is investigated.

EXAMPLE 1

The alloy for the following test is prepared as follows: Copper and titanium are melted under vacuum (this may also be done in pure argon). Titanium content is selected in the neighbourhood of the eutectic, that is, 20% to 30% titanium. The melting point of the pre-alloy thus formed may be lowered by the addition of zinc. The solidified pre-alloy is dissolved in molten zinc. A quantity of the pre-alloy is used so that the concentration of titanium in the final alloy is between about 0.05% to 1%.

Bend Test with	Material Without Further Treatment	After Annealing 2 hours at 200° C.
High purity zinc	12—14	1—2
Alloy	3—5	5—8

The numbers give the numbers of bends until breaking. The titaniferous crystal is medium fine in texture and is often acicular. In the annealed material, many recrystallized zinc crystals may be seen.

EXAMPLE 2

An alloy is prepared as in Example 1 except that the copper that is fused with titanium into the pre-alloy is contacted with hy-

drogen gas and/or ammonia gas.

It should be noted that it is immaterial whether the copper melt is treated with hydrogen gas or gaseous ammonia and the titanium then introduced into the saturated melt, or whether the melt and/or the titanium are gas treated separately. In either case the hydrogen is bound chemically to the titanium.

Bend Test with	Material Without Further Treatment	After Annealing 2 hours at 200° C.
Alloys (numbers of bends until breaking)	15—20	25—30

The titaniferous crystals appear spherical in form and are extremely finely divided. They do not change their outer appearance during annealing. No recrystallization appears and during annealing the plasticity of the alloy increases greatly.

Comparison of Examples 1 and 2 shows that the pure titanium additives are relatively ineffective but when combined with hydrogen and nitrogen in accordance with the present invention, marked improvement is obtained. This result was achieved in spite of the power-

ful annealing treatment of the zinc alloys which range from 100°C to as high 300—350°C.

- 5 As previously noted, in plumbiferous zinc alloys such as those obtained from a zinc spelter base, the separation of lead in small droplets upon solidification causes an irregular dispersion of lead in the alloy and explains why malleable materials with a spelter
- 10 base always have poorer ductility than those

with a zinc powder base Even when using zinc spelter, the present alloys offer a much better plasticity than could previously be obtained:

EXAMPLE 3

Alloys were prepared as in Example 2 and formed in a 0.6 mm sheet after annealing at 300°C. for two hours. The following bend test results were obtained:

Bend Test No.	Material Without Further Treatment	After Annealing 2 hours at 300° C.
20 Alloy from spelter	5—6	12—15
Zinc Spelter	2—3	0—1

After steam treating for ten days the alloy showed no intercrystalline corrosion and no impairment of its properties in general.

EXAMPLE 4

- 25 The following example illustrates in tabular form the comparative values of the creep resistance of various high purity zinc alloys.

- 30 Lengthy creep testing was conducted on 0.6 mm ribbon strips parallel to the direction of rolling with a total strip length of 600 mm.

The strips were stretched under tension by a lever arm with a ratio of 1:10. The reading of the amount of stretch can be taken from the long lever arm up to 200 mm, i.e. up to 3.3%

Comparative studies were made on: high purity zinc, high purity zinc with 1% copper (ZnCu 1), high purity zinc with 0.15% titanium (ZnTi15) and a complex zinc-copper-titanium alloy (STZ), as follows:

	High purity zinc	ZnCu 1	ZnTi 15	ZnCuTiMn (STZ)
Zn%	99.99	99	99.85	High purity zinc
Cu%	—	1	—	0.4 — 0.8
Ti%	—	—	0.15	0.1 — 0.2 preferably 0.15%
Mn%	—	—	—	0.1 — 0.2

and the same alloy in the annealed state (STZ annealed).

- 45 Here the titanium present, in accordance with the invention, in the alloy designated as STZ, contains about 5 atomic percent hydrogen or about 20 atomic percent nitrogen or an equivalent amount of oxygen dissolved in the solid solution or bound with the titanium.

The creep resistance of strips of high purity zinc and various alloys, stretched parallel to the direction of rolling, in days 1% elongation are shown in the following table, in which the figures given in brackets are obtained by interpolation:

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Material	2	Load Kg/mm ²			10	12	14
		4	6	8			
Zinc Powder	40	0.63	0.01	—	—	—	—
ZnCu 1	(1600)	32.00	1.0	0.02	—	—	—
Zn with 0.15% Ti	—	(3200)	126.00	3.20	0.04	—	—
ZnTi with Cu, Mn (STZ)	—	—	—	350.00	10.00	0.2	—
ZnTi with Cu, Mn annealed and re-rolled (STZ)	—	—	—	—	(1000)	20.00	0.63

In particular, the table shows that in the alloy STZ according to the invention, ZnTi with Cu, Mn, a load of 8 kg/mm² is possible with a creep rate of 1% a year (350 days). Here, however, the maximal possibilities for improved quality are not yet utilized. To obtain a creep resistance corresponding to a tension of 1% a year, therefore, the limit of load is shown in kg/mm².

High purity Zinc	ZnCu 1	ZnTi 15	ZnTiCuMn (STZ)	Annealed and rerolled: ZnTiCuMn (STZ)
1.2	2.8	5.30	8.0	10.5 ... kg/mm ²

The load capacity of the STZ alloy corresponds to 60% of the proportional limit, while alloys of the ZnCu 1 type with equal proportional limit and hardness can bear only loads of 20% of the value noted.

It has been found in long term practical studies that the titaniferous STZ-zinc alloys in rolled sheet form behaved even more favourably while the titanium free alloys behaved even more unfavourably than was previously estimated.

It is also interesting to note that the strain ratio in a zinc alloy in accordance with the present invention such as the alloy designated above as STZ, a stress of 120% is reached before fracture, while the stress in the area adjacent to the rupture rises to 200%.

WHAT WE CLAIM IS:—

1. A titanium zinc alloy which contains more than 50% by weight of zinc, the balance apart from unavoidable impurities being titanium and from 1 to 67 atomic per cent of hydrogen or nitrogen or oxygen or a mixture of two or more of these elements, based on the quantity of titanium, which hydrogen, nitrogen or oxygen is combined with the titanium, is dissolved in the solid solution or is in part combined and in part dissolved.

2. An alloy as claimed in claim 1 containing from 0.01 to 1% by weight of titanium based on the weight of the alloy.

3. An alloy as claimed in claim 1 or claim 2, in which up to 50% of the titanium is replaced by zirconium or hafnium or a mixture thereof.

4. An alloy as claimed in any one of the preceding claims in which the zinc is present as refined zinc, spelter or a mixture thereof.

5. An alloy as claimed in any one of the preceding claims also containing from 0.1 to 10% by weight of copper.

6. An alloy as claimed in claim 5 in which up to 50% of the copper is replaced by manganese.

7. An alloy as claimed in claim 6 containing from 0.1 to 0.2% by weight of manganese.

8. An alloy as claimed in any one of the preceding claims also containing from 0.1 to less than 50% by weight of aluminium.

9. Alloys as claimed in any of the preceding claims which have been subjected to a cold deformation at between 20 to 100°C. and an annealing treatment at between 100°C. and 350°C.

10. Titanium zinc alloys as claimed in any of the preceding claims substantially as herein described.

11. Titanium zinc alloys as claimed in any of the preceding claims substantially as herein described with reference to any one of the Examples.

12. A process for the production of alloys as claimed in any of the preceding claims in which a pre-alloy prepared by melting solid titanium into liquid copper is treated with a gas as specified in claim 1 or a gas yielding hydrogen under the treatment conditions, and the pre-alloy is then added to the zinc melt.
13. A process as claimed in claim 12 in which the pre-alloy is treated with hydrogen or gaseous ammonia.
14. A process for the production of an alloy as claimed in any of claims 1 to 11 in which liquid copper is treated with a gas as specified in claim 1 or a gas yielding hydrogen under the treatment conditions, titanium is added to the copper melt and the pre-alloy so formed added to the zinc melt.
15. A process as claimed in claim 14 in which the copper melt is treated with hydrogen or ammonia.
16. A process as claimed in claim 14 or claim 15 in which the titanium is treated with the gas before being added to the copper melt.
17. A process as claimed in any of claims 12 to 16 in which the melting point of the pre-alloy is lowered by the addition of zinc.
18. A process as claimed in claim 17 in which the zinc is added after the copper-titanium melt has been treated with the gas.
19. A process for the production of alloys as claimed in claim 1 substantially as herein described with reference to any one of the Examples.
20. Alloys when made by a process as claimed in any of claims 12 to 19.

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